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New Encoding Schemes with Infofuses

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Introduction

Information technology is an area of such broad importance that even small enhancements to existing methodologies can be useful. Most information derived from *chemistry* – and especially from some form of analysis – proceeds by a path in which a sensor (e.g., an analytical instrument), using electrical power, generates information, which is then encoded and transmitted in a separate step, again using electrical power, to a separate unit (which may be local or distant) for processing and interpretation. We^[1,2] and others^[3-6] are exploring schemes in which information is transmitted directly, without using electrical energy. Such schemes have the potential to be useful where electrical power is not reliably available, or where other constraints (e.g., size) argue for other types of solutions.

Infofuses are a new system for non-electronic communications that uses the multiplexing of frequencies enabled by chemistry.^[1,2] This paper describes non-binary encoding schemes for infofuses which allow a single pulse of light to encode each of the alphanumeric characters. This work demonstrates a physical implementation of a new, information-dense, encoding scheme, and is important to materials scientists and engineers interested in research at the interface between information science and chemistry. We refer to this area as *infochemistry*.

We consider an elementary system for transmitting information to have seven steps: i) Assembling the message (either by writing it, or by collecting it from a sensor), ii) Encoding the information in a form that can be transmitted, iii) Transmitting the information, iv) Receiving the information, v) Decoding the information, vi) Interpreting the decoded information, vii) Acting on this information.

Infochemistry combines the attractive features of chemical systems (high energy density, self-powered operation, long storage times for energy, facile coupling with certain kinds of chemical sensing) with the encoded storage and transmission of information.

Infochemical systems offer the opportunity to implement, in a physical system, encoding schemes that are more information-dense than simple binary by transmitting information optically using multiple (rather than two) states (e.g., multiple intensities and multiple wavelengths). Multiple-state pulses can give a higher density of information per clock cycle (although at increased complexity, with increased error rates, and lower bit rate) than the binary systems now almost universally used.^[7,8]

We have developed two infochemical systems that use chemical interactions and reactions (and that do not require electrical power in the transmission step) to transmit encoded messages as optical pulses. One is based on strips of flammable polymer (nitrocellulose) with thermally emissive salts (infofuses) patterned onto it.^[1,2] The second is a microfluidic device that shutters light (a droplet shutter), and capitalizes on the high frequency stability of the rate of generating bubbles by a flow-focusing nozzle.^[9] In this latter system, the combination of optically transparent droplets and windows serve as optical shutters to encode information.

Upon ignition of one end of an infofuse, the flame front (at a temperature of $\sim 1000^{\circ}\text{C}$) propagates along the fuse at a constant rate ($2 - 3 \text{ cm/s}$ in the systems we use). As this propagating hot zone reaches each spot of thermally emissive salts, it emits light at wavelengths characteristic of the thermal emission of the atoms present in the spot.^[10,11] The spatial pattern of emissive salts is therefore transduced (in the optical far-field) into a sequence of optical pulses at different wavelengths, ordered in time. With current systems, the intensity of isotropic radiation from a spot of $\sim 1 \text{ mm}^2$ is such that the emission can be detected and correctly characterized from any angle at distances as great as $\sim 600 \text{ m}$ at night.^[12]

The design of infofuses we reported previously used three thermal emitters to encode and transmit information: the three alkali metals (Li, Rb, and Cs); we chose these three

because we could not detect them as background in burning films of pristine nitrocellulose.^[1,2,13] In this work, we added Na (NaClO₄) at the same concentration to each emissive spot to provide an internal standard that allowed normalization of the intensity of the pulse. We designed an encoding scheme that assigned alphanumeric characters to combinations of unique optical pulses using three distinct emitters: we could generate seven ($2^3 - 1$) unique optical pulses. Using two consecutive pulses (giving a total of 49 unique two-pulse combinations), we encoded each alphanumeric character.

Although this encoding scheme for transmitting alphanumeric information with infuses is effective, it has two disadvantages: i) It limits the maximal frequency at which the infuse can transmit alphanumeric information to half the frequency at which we generate pulses (which is set by rate of propagation of the flame front and by the spacing between emissive metal salts). ii) Consecutive pulses from the same combination of emitters is a source of error in decoding the message that an infuse transmits; if the pulses are close together, it can be difficult to determine if they are from the same spot or from consecutive spots of the same composition. With the 2-pulse encoding scheme, there is a 2% ($1/49$) probability of two consecutive pulses having the same combination of emitters.

By encoding each character with a single optical pulse, we can increase the maximal frequency that information is transferred by a factor of two over the two-pulse scheme, and also reduce errors in the detected signal. The frequency we achieved in the demonstration system we describe in this paper is ~12 characters/sec, detected at a distance of ~ 1 m from the transmitter.

In this paper, we designed and demonstrated two different encoding schemes for infuses that transmit each alphanumeric character with a single optical pulse (**Figure 1**):

i) a scheme that is binary (0,1) in the intensities of light emitted from six (Li, K, Rb, Cs, Sr, Ca) thermal emitters; ii) a scheme that is binary and ternary (0, 1, 2) in the intensities of light emitted from four (Li, K, Rb, Cs) thermal emitters.

Results and Discussion

Simultaneous Binary Emission Using Six Thermal Emitters Can Encode All Alphanumeric Characters. To encode alphanumeric characters with a single optical pulse, we developed a new encoding scheme that uses six thermally emissive metal perchlorate salts: in addition to lithium, rubidium, and cesium, (the combination we used previously),^[1,2] we included strontium, calcium, and potassium.^[14]

The amount of light that reaches the detector depends on the position of the flame front of the fuse and the quantity of emissive salts deposited on the fuse. To correct for observed differences in intensity between pulses from these errors due to variations in these parameters, each emissive spot also contained 0.2% (w/v) of sodium perchlorate as an internal standard. We used the sodium emission (which was ~3 times greater than the background sodium intensity in the nitrocellulose fuse) to correct the intensities for dividing the intensity of light each encoding metal (I_x) emitted by the intensity of emission from sodium (I_{Na}).

Formally, six independent emitters that are binary (0,1) in their intensity yield 63 ($2^6 - 1$, assuming there should always be at least one element emitting during a pulse) unique combinations of emission spectra. In practice, overlaps between the emission spectra of some of the emitters exclude some combinations from use in the infofuse. In particular, the emission from strontium (**Figure 2**) is broad: it stretches between ~600 nm and ~700 nm and overlaps with the emission from calcium at 620 nm and lithium at 670 nm. We therefore excluded calcium and lithium from any encoding pulse that contained strontium; this

encoding scheme has 39 unique combinations of emitters that are useful for transmitting information. $2^5 - 1$ of these combinations do not use Sr, while 8 of these combinations (2^3) are those that are possible (i.e., those that do not use Ca or Li) when Sr is present. This scheme can therefore encode 26 letters (A-Z), 10 digits (0-9) and three other characters, each with a single optical pulse (**Figure 3**).

The presence of potassium in this encoding scheme poses another challenge: emission from potassium (as well as sodium) is present when nitrocellulose burns. When we did not intentionally add K to the emissive spot, the ratio of the height of the emission peak from potassium to that from sodium (I_K/I_{Na}) was $\sim 0.2 \pm 0.1$, whereas when we did intentionally add K to the emissive spot, $I_K/I_{Na} = \sim 2.0 \pm 0.1$ (**Figure 4**).^[15] Therefore, the mean values of I_K/I_{Na} of the two states are substantially separated with each other.

We designed the encoding scheme (**Figure 3**) such that the clearest signals encoded the most common letters used in the English language, according to the following guidelines: i) single-emitter signals encoded the six most common letters: (E, T, A, O, I, N). ii) combinations that only use the alkali metals not found in nitrocellulose (Li, Rb, Cs), encoded the next four letters (S, H, R, D). iii) remaining combinations used one or more of the “non-ideal” emitters (K, Sr, Ca).

Using this encoding scheme, we transmitted the message “A QUICK BROWN FOX JUMPS OVER THE LAZY DOG” (**Figure 4**). This sentence is a useful test message because it contains each letter of the English alphabet at least once. The asterisks in Figure 4 highlight emitted peaks due to emission from Sr that are also detected at the wavelengths where Ca and Li emit (620 nm and 670 nm).

Alkali metals can encode alphanumeric information with the wavelengths and intensities of optical pulses. Infochemical systems have the characteristic that they can encode and transmit information in different parameters simultaneously. In this section, we

describe infofuses that transmit each alphanumeric character with a single pulse using both the wavelength of emitted light, and its intensity relative to an internal standard (Na).

We chose the alkali metals (as opposed to the alkaline earth metals in the previous section) for this demonstration since the linewidths of their emission spectra are narrow (< 2 nm); this feature increases signal-to-noise relative to emissions of other possible elements.

Four emitters (Li, K, Rb, Cs), each emitting with one of three intensities (0, 1, 2), yield $80 (3^4 - 1)$ unique optical pulses. To ensure high signal-to-noise of the peak intensity, however, we restrict which of these combinations encode information: i) The background emission from potassium from burning nitrocellulose film limits the signal-to-noise of potassium to about 10:1. We therefore treated potassium as a binary (0, 1), not a ternary, encoding element. ii) We adjusted the emitted intensity of the metals by changing their concentration in the solution (**Table 1**) that we deposited on the infofuse, relative to intentionally added sodium perchlorate (at a constant value of 0.5% w/v).

This restriction leaves $53 [(2 \times 3^3) - 1]$ unique optical pulses that can encode alphanumeric characters. From these remaining combinations, we designed an encoding scheme (**Figure 5**) for 40 alphanumeric characters with the following guidelines: i) Single-emitter signals at high concentration (2 for Li, Rb, or Cs, and 1 for K) encoded E, T, A, and O. ii) Two-wavelength pulses with at least one emitter at high concentration encoded I, N, S, H, R, D, L, C, U, M, and W. iii) Three-wavelength pulses that did not include potassium, and with at least 1 emitter at high concentration encoded F, G, Y, P, and B. iv) Two-wavelength pulses with both emitters at low concentration encoded V, K, J, X, Q, and Z. v) Three-wavelength pulses that included potassium encoded numbers. vi) One- or three-wavelength pulses, with all emitters at low concentration, encoded the four special characters.

Using this encoding scheme based on both wavelength and intensity, we encoded and transmitted the message “A NEW DEVICE TO TRANSMIT DATA” (**Figure 6**). The

standard deviation in intensities relative to the internal standard at the peak of each optical pulse was approximately 10% of the mean, while the means of the two emitting populations (“2” and “1”) for each of the emitters are separated by at least two times the sum of the standard deviations for the two intensities.

In conclusion, we have two described approaches that improve a previously described system of “infofuses”. By employing a system that is binary in intensity using six different thermally emissive salts, or a system that can be binary and ternary in intensity using four different thermally emissive salts, we encoded and transmitted alphanumeric information with individual optical pulses. New encoding schemes allowed us to improve the density of the information, and to lower the error rate, relative to a previously described system.

The improved functionality and potential of infofuses described in this work to encode and transmit information without electrical power, could ultimately allow new protocols for sensing and manipulating data from sensors.

Experimental

Nitrocellulose was obtained from Scientific Polymer Products (powder) or Whatman (membrane filter). All metallic salts were obtained from either Alfa Aesar or Sigma-Aldrich in the highest available purity. All aqueous solutions were prepared with water purified and deionized by a Millipore system.

Sheets of nitrocellulose were prepared by pouring ~ 50 mL of a 5% (w/v) solution of nitrocellulose (in acetone) into a 5 cm × 30 cm polyethylene box, closing the lid, and allowing the solvent to evaporate over a few days at room temperature. The resulting sheets of nitrocellulose were either optically clear or slightly translucent. The sheets were then cut into strips with width of ~1 mm using a desktop rotary paper trimmer.

We patterned strips of nitrocellulose with emissive salts via manual spotting. A solution for each of the combinations of unique emitters (Li, Rb, Cs, K, Sr, and Ca) of emissive salts for manual spotting were prepared by dissolving 1.0% (w/v) (Li), 0.1% (w/v) (Rb), 0.2% (w/v) (Cs), 0.5% (w/v) (K), 2.5% (w/v) (Sr), and 1.0% (w/v) (Ca) of alkali perchlorate in a stock solution of 0.2% sodium perchlorate in water. Each spot of emitters (~100 nL) was deposited onto the strip of nitrocellulose with a micropipettor (VWR). After all the desired spots were deposited onto the fuse, it was dried in ambient and in an oven at ~50°C for 30 minutes until the water from the deposition of emitters had evaporated.

For spectroscopic detection, a system of four lenses collected and focused the light emitted from a burning infofuse. Two 1-inch diameter fisheye lenses collected light from the entire area occupied by the infofuse; a focusing lens directed the collected light into a 1 mm-diameter multimode optical fiber (Ocean Optics) that was equipped with a collimating lens. Light from this fiber was coupled to a HR2000+ high resolution CCD spectrometer (Ocean Optics), which was connected to a PC with a USB cable and controlled by software (SpectraSuite) supplied by Ocean Optics. All emission spectra from infofuses were collected with an integration time of 10 ms, at a rate of 100 spectra/s. The distance between the detector and the burning infofuse was typically 1 m.

Acknowledgements

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- [14] We excluded other potential thermal emitters (copper, indium, thallium, boron, lead, arsenic, mercury, silver, barium, aluminum) from the code because they either showed insufficient intensity in emission or overlapped with many of the other alkali metal emitters.
- [15] When potassium nitrate, with higher solubility in water than potassium perchlorate, was used, we could increase the value of I_K/I_{Na} up to 3.2 ± 0.2 .

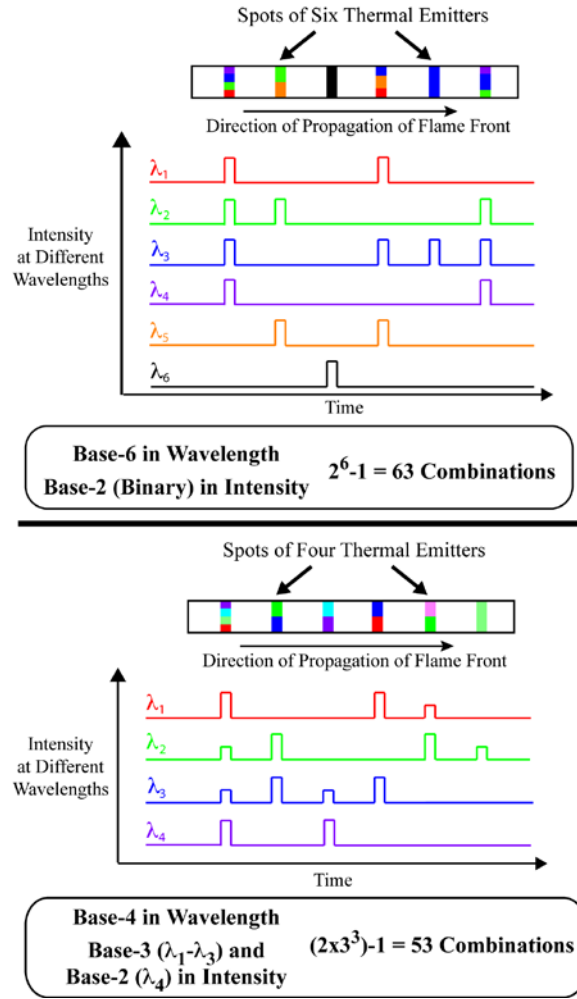


Figure 1. Schematic diagram of infofuses that can encode and transmit alphanumeric information with individual optical pulses. *Top:* A schematic description of a binary system in intensity that uses six different thermally emissive salts. *Bottom:* A schematic description that is binary and ternary system in intensity, and that uses four different thermally emissive salts.

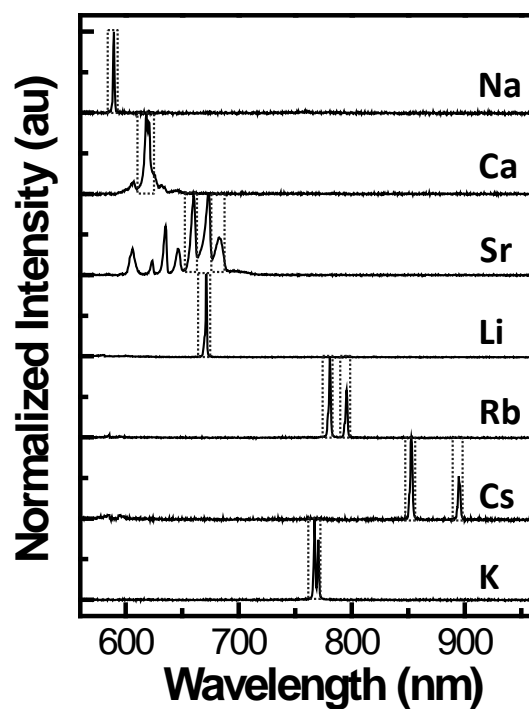


Figure 2. Normalized thermal emission spectra (between 550 and 950 nm) of sodium, calcium, strontium, lithium, rubidium, cesium, and potassium perchlorate deposited on a burning infofuse. The boxes with gray dashed borders show the areas of the emission spectrum that we integrated to determine the intensity of emission from each metal salt. We avoided overlaps between Sr, Ca, and Li by excluding combinations of Ca and Sr, and Li and Sr, as in Figure 3.

	Encoded Pulse							Encoded Pulse					
	Sr	Li	K	Rb	Cs	Ca		Sr	Li	K	Rb	Cs	Ca
A	0	1	0	0	0	0							
B	0	1	0	0	0	1							
C	0	0	1	0	1	0							
D	0	1	0	1	1	0							
E	0	0	0	1	0	0							
F	0	0	1	1	1	0							
G	0	1	1	1	0	0							
H	0	1	0	1	0	0	0	0	0	0	1	1	1
I	1	0	0	0	0	0	1	1	0	1	1	0	0
J	0	0	1	0	0	1	2	1	0	1	0	1	0
K	0	0	0	1	0	1	3	0	1	0	1	1	1
L	0	0	1	1	0	0	4	0	1	1	0	0	1
M	1	0	0	0	1	0	5	0	1	0	1	0	1
N	0	0	0	0	0	1	6	0	1	0	0	1	1
O	0	0	1	0	0	0	7	0	0	1	1	1	1
P	0	1	1	1	1	0	8	1	0	1	1	1	0
Q	0	0	1	0	1	1	9	0	1	1	0	1	1
R	0	1	0	0	1	0	.	0	1	1	1	0	1
S	0	0	0	1	1	0	!	0	0	1	1	0	1
T	0	0	0	0	1	0	?	0	1	1	1	1	1
U	1	0	0	1	0	0							
V	1	0	1	0	0	0							
W	0	1	1	0	0	0							
X	0	0	0	0	1	1							
Y	0	1	1	0	1	0							
Z	1	0	0	1	1	0							

Figure 3 Single-pulse encoding scheme for 39 characters that uses six thermally emissive salts to encode and transmit information. Spectral overlap between Sr and Ca or Li precluded those two emitters from being used with Sr.

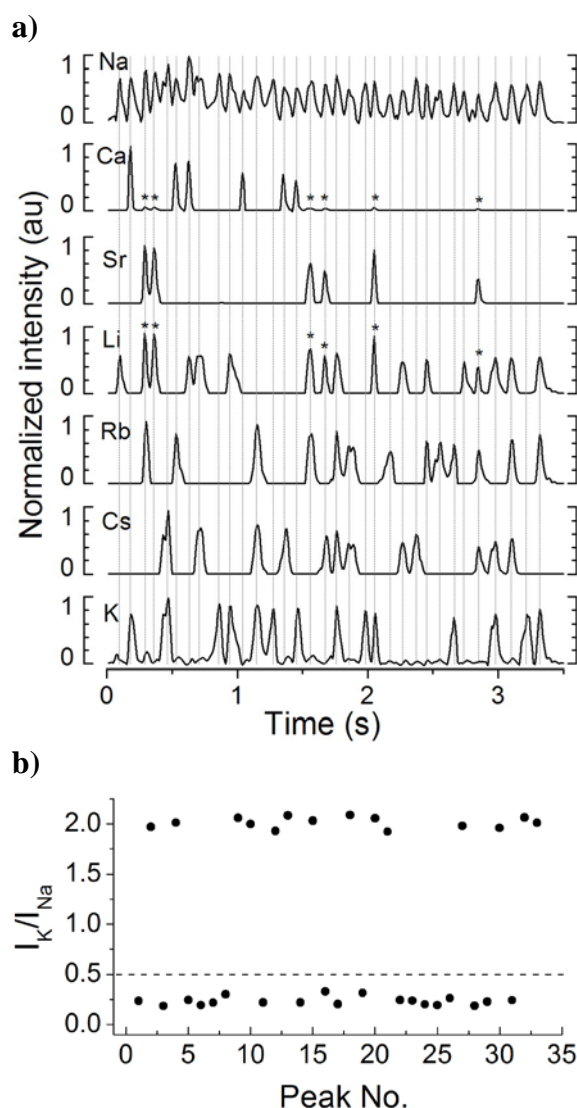


Figure 4 Transmission of the message “A QUICK BROWN FOX JUMPS OVER THE LAZY DOG” using the single-pulse encoding scheme from Figure 3. a) Normalized intensity of each of six encoding emitters (I_X) and the internal standard (I_{Na}). Note that when Sr emits, it emits at the wavelengths at which Li and Ca emit (asterisks). b) I_K/I_{Na} at each of the peaks. The grey dashed line indicates the threshold for potassium emitting as an encoding atom. The stability of the ratios I_K/I_{Na} demonstrates the value of using Na emission as a internal standard.

	Encoded Pulse					Encoded Pulse			
	Li	K	Rb	Cs		Li	K	Rb	Cs
A	0	0	0	2					
B	1	0	2	1					
C	0	0	1	2					
D	1	0	2	0					
E	2	0	0	0					
F	2	0	2	1					
G	2	0	1	2					
H	0	1	2	0	0	1	1	2	0
I	2	0	2	0	1	2	1	1	0
J	1	0	1	0	2	2	1	2	0
K	1	1	0	0	3	1	1	0	2
L	1	0	0	2	4	2	1	0	1
M	0	0	2	1	5	2	1	0	2
N	2	0	0	2	6	2	1	1	1
O	0	1	0	0	7	1	1	1	0
P	1	0	1	2	8	0	1	1	1
Q	0	1	1	0	9	1	1	0	1
R	0	1	0	2	.	1	0	0	0
S	2	1	0	0	!	0	0	1	0
T	0	0	2	0	?	0	0	0	1
U	2	0	1	0	@	1	0	1	1
V	0	0	1	1					
W	2	0	0	1					
X	1	0	0	1					
Y	2	0	1	1					
Z	0	1	0	1					

Figure 5. Single-pulse encoding scheme for 40 characters that uses the intensities of four thermally emissive alkali metal perchlorates relative to an internal standard (Na) to encode and transmit information. In this scheme, the intensities of Li, Rb, and Cs are ternary (0,1,2), while the intensity of K is binary (0,1).

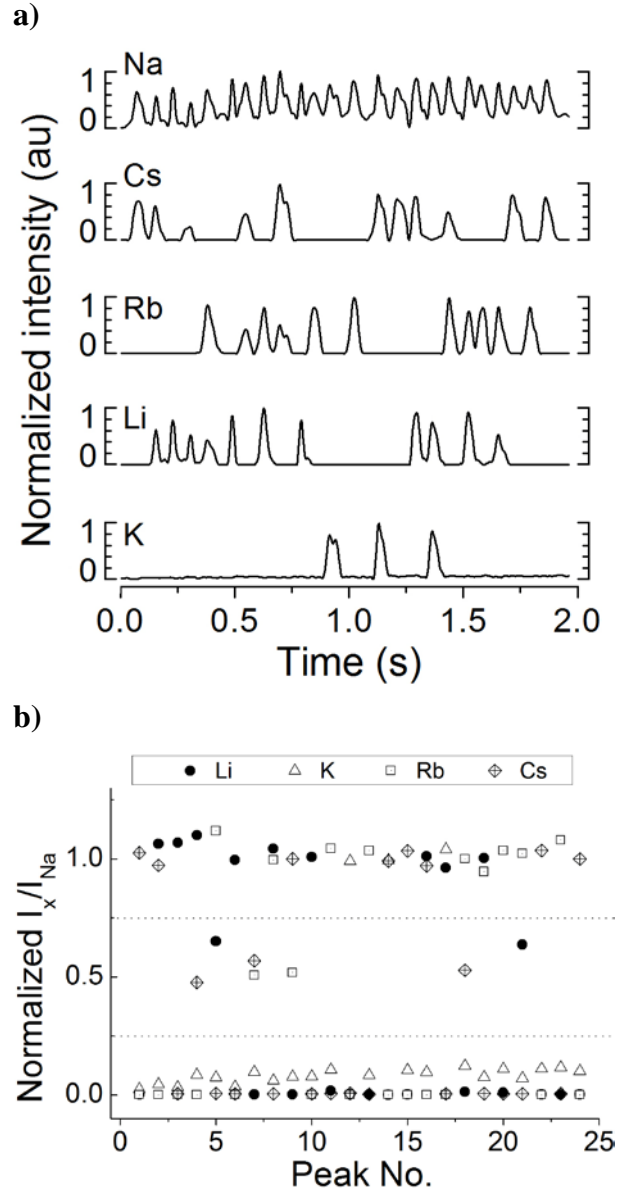


Figure 6. Transmission of the message “A NEW DEVICE TO TRANSMIT DATA” using the encoding scheme from Figure 5. a) Normalized output of the encoded burning infofuse at the emission wavelengths of each of the alkali metals. b) Relative intensities of each normalized pulse processed by comparing to the intensity of emission from the internal standard (sodium perchlorate). The horizontal grey dashed lines show the boundary between intensity levels of “2” and “1”, and between intensity levels of “1” and “0” for Li, Rb, and Cs.

Table 1. Percentage (w/v, g/100 mL of H₂O) of the five alkali perchlorate salts in the aqueous solutions we used to pattern infofuses, that when burned transmitted an intensity of “0”, “1”, or “2”. Sodium is an internal standard at the same concentration (0.5% w/v) in all solutions. *a* Not used: we restricted potassium to transmit in binary only (“0” or “1”).

Alkali Perchlorate	Intensity Value		
	0	1	2
Lithium	0.0	0.4	1.2
Sodium	0.5	0.5	0.5
Potassium	0.0	1.0	<i>a</i>
Rubidium	0.0	0.2	0.8
Cesium	0.0	0.2	0.8

ToC

Single-Pulse Encoding for “Infofuse”: Non-binary encoding schemes for “Infofuses” – chemically based systems for non-electronic communication – allow a single pulse of light to encode and transmit each of the alphanumeric characters.

Keywords: Infochemistry, infofuse, non-binary

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New Encoding Schemes with Infofuses

